

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

The catalyst used in this work was a commercial bimetallic palladium-silver catalyst supported on alpha alumina (Pd-Ag/ α -Al₂O₃), supplied by National Petrochemical Public Company Limited. Table 3.1 summarizes the catalyst characterization data.

Table 3.1 Catalyst characterization data

Pd (wt %)	0.030 \pm 0.005
Ag (wt %)	0.235 \pm 0.025
Al ₂ O ₃ (wt %)	99.6 \pm 0.1
Density (g/cm ³)	0.70 \pm 0.05
Surface area (m ² /g)	30
Pore volume (cm ³ /g)	0.45 \pm 0.05

Alpha alumina (α -Al₂O₃) pellets, 2.4 mm in diameter obtained from Nissan Girdler Catalyst Co., Ltd., were used for blank studies.

Gases used in this work were

- Acetylene 5.01% balanced with nitrogen
- Ethylene 41.23% balanced with nitrogen
- Hydrogen 2.62% balanced with nitrogen
- Ultra high purity (UHP) hydrogen
- Ultra high purity (UHP) nitrogen

All gases were obtained from Thai Industrial Gas Public Co., Ltd. (TIG).

3.2 Catalyst Preparation

Due to the high activity of the Pd-Ag/Al₂O₃ catalyst, the catalyst used in these experiments had to be diluted to attain a differential reactor operation. Pd-Ag/Al₂O₃ pellets were ground with blank alumina pellets in a high speed centrifugal ball mill, and then the mixture was sieved with a 80/120 mesh screen.

3.3 Apparatus

The experimental system is shown in Figure 3.1. The system was divided into three parts: i) gas blending system; ii) the differential flow reactor and; iii) gas chromatograph for analysis of products.

3.3.1 Gas Blending System

The flow rate of each gas was controlled by mass flow transducers and controllers model 840 from Sierra Instrumental Inc. All the

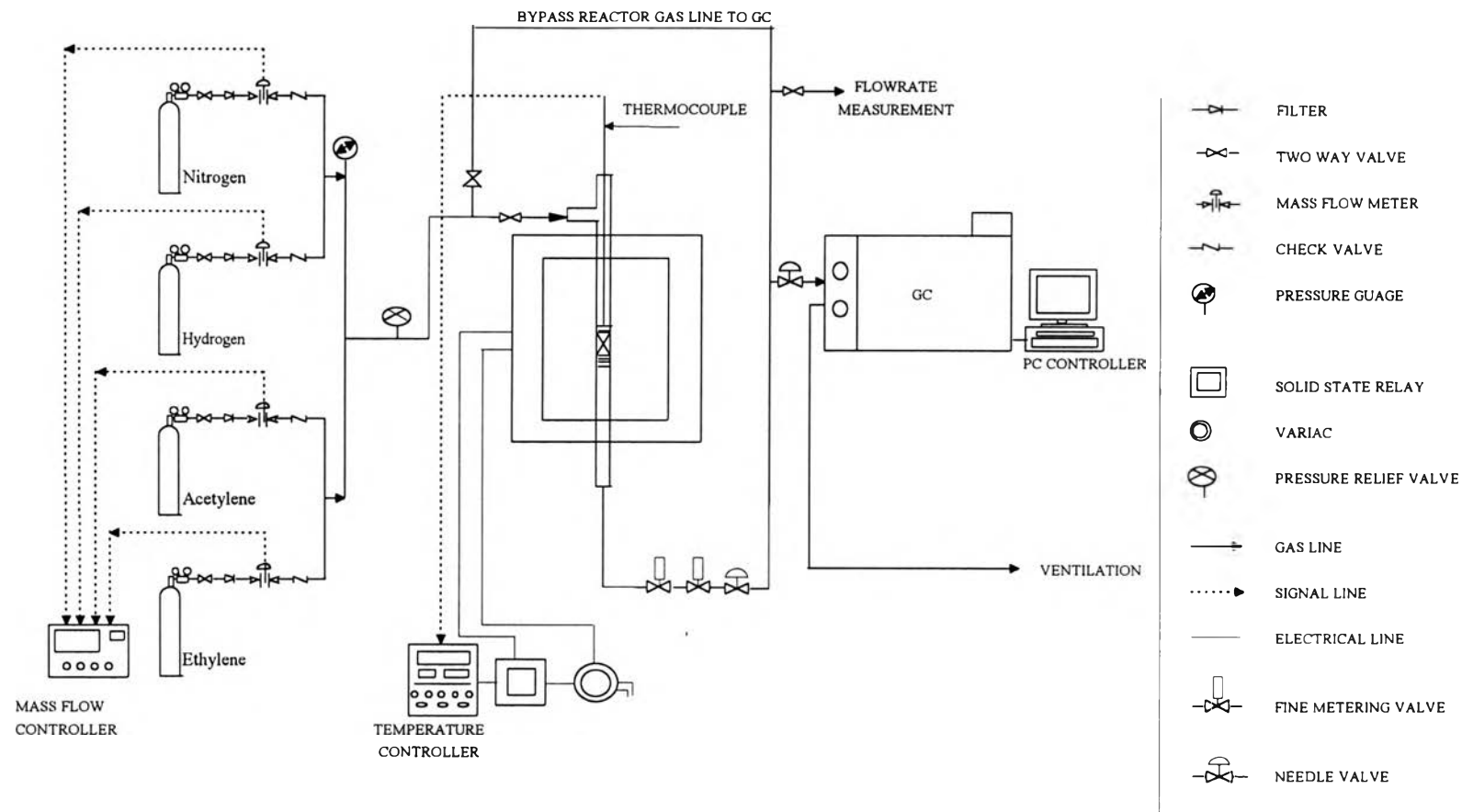


Figure 3.1 Schematic flow diagram of the experimental system.

reactant gases were passed through 7 micron filters and the mass flow meters, and mixed before feeding into the reactor.

3.3.2 Differential Flow Reactor

The reactor was made from three Swagelok unions (1/4 inch diameter). The catalyst was packed between two plugs of quartz wool. The reactor was placed in an electrical heater. The reaction temperature was controlled by a PID controller, model UP27 manufactured by Yokogawa Instruments. Two fine metering valves and one needle valve were installed to adjust and maintain the pressure in the reactor at 18 kg/cm² (255 psi).

3.3.3 Analytical Instrumentation

A Hewlett Packard 5890 series II gas chromatograph equipped with thermal conductivity detector (TCD) was used for gas composition analysis. The analysis was conducted using a Carboxen 1004 micro-packed column at the set temperature of 170, 250 and 150 °C for column, detector, and injector, respectively. GC peaks were calibrated using known standards.

3.4 **Reaction Studies**

The reaction studies were divided into three parts: i) external limitation; ii) deactivation studies and; iii) acetylene hydrogenation in the presence of ethylene.

Fresh catalyst of 0.1 g was used in all experimental runs. This 0.1 g catalyst contained 0.00625 g of actual catalyst and 0.09375 g of blank alumina as diluent. First, the catalyst was pretreated for 2 hours by 15 mole % hydrogen at 200 °C. After the pretreatment, the temperature was cooled down

in a flow of pure nitrogen to the reaction temperature. The reactant gases, set at the desired composition, were allowed to enter the system. The pressure was built up and maintained at 18 kg/cm^2 throughout the experiment. The outlet gases were injected into the GC to check the composition until the steady-state condition was reached.

3.4.1 External Limitation

Tests of external limitations were conducted to find the flow rate in the region of no external limitation. The reactant compositions used were fixed at 2 mole % hydrogen and 1 mole % acetylene. The reaction temperature was $80 \text{ }^\circ\text{C}$. The feed flow rate used was varied at 150, 200, 250, 300 and 400 ml/min.

3.4.2 Deactivation Studies

For the deactivation studies, hydrogen concentration and reaction temperature were maintained constant at 2 mole % and $80 \text{ }^\circ\text{C}$. The acetylene concentration was varied at 0.4, 1.5, 2.0, 3.0 and 4.0 mole %.

3.4.3 Acetylene Hydrogenation in the Presence of Ethylene

Two sets of six experiments were performed at $80 \text{ }^\circ\text{C}$ with 25 mole % of ethylene. The hydrogen concentration were 1 and 2 mole % for the two sets. The acetylene concentration was varied at three different values as shown in Table 3.2

Table 3.2 Operating conditions for acetylene hydrogenation in the presence of ethylene

Hydrogen, mole %	2	1
Ethylene, mole %	25	25
Temperature, °C	80	80
Acetylene, mole %	0.5, 1.0, 1.5	0.25, 0.5, 0.75
Ethylene/ Hydrogen	25/2	25/1
Ethylene/ Acetylene	50, 25, 16.6	100, 50, 33.3

3.5 Temperature Programmed Desorption (TPD)

Temperature programmed desorption was carried out in a Micromeritics TPD/TPR 2900 instrument with the temperature range of 40-600 °C to study the effect of hydrogen reduction condition and exposure time. The fresh catalyst was reduced in pure hydrogen at 200 °C. The reduction time was varied from 2, 3 to 4 hours. Then, the catalyst was flushed with nitrogen and cooled down to room temperature. Hydrogen was exposed to the catalyst at two different exposure times, 15 and 30 minutes. After that, the TPD was started with the heating rate of 10 °C/min in nitrogen atmosphere.

3.6 Catalyst Regeneration

After loading 0.1 g of fresh catalyst into the reactor, the catalyst was reduced at 200 °C by 15 mole % hydrogen for 2 hours, and then cooled down to 80 °C by pure nitrogen. After that, reactant gases, 2 mole % hydrogen and 1

mole % acetylene, were allowed to flow into the reactor and then the hydrogenation reaction was allowed to take place for 3 hours.

The catalyst was then regenerated. The bed was heated to 180 °C by pure nitrogen and then 15 mole % hydrogen was fed to the reactor for 1 hour to regenerate the spent catalyst.

This procedure was repeated for 3 cycles at three different operating conditions. The regeneration temperature was varied from 180, 200 to 300 °C and the regeneration time was varied from 1, 2, to 3 hours.

Fresh catalyst and catalyst regenerated at 200 and 300 °C were then analyzed for their pore volumes and pore sizes by BET method.

3.7 Evaluation of the Experimental Data

In case of ideal mixing and negligible influence of transfer limitation, the experimental conversion rates of a reactant j per unit mass of catalyst can be evaluated from

$$R_j = (y_{j,in}F_{in}/W)\zeta_j \quad \dots\dots (1)$$

where

- $y_{j,in}$ = mole fraction of reactant j in the feed stream;
- F_{in} = total feed stream flow rate;
- W = weight of catalyst;
- ζ_j = degree of conversion of component j .

The degree of conversion of component j can be defined as

$$\zeta_j = (F_{j,in} - F_{j,out})/F_{j,in} \quad \dots\dots (2)$$

where $F_{j,in}$, $F_{j,out}$ = input and output reactant j flow rate,
respectively.